Preface

It is fitting that this issue of the *IBM Journal of Research and Development*, devoted to electrochemical science and technology in IBM, was planned in 1991, the 200th anniversary of the birth of Michael Faraday. Faraday was a seminal figure in what has developed into several separate disciplines in physics and chemistry, and he received numerous tributes in the respective journals of these disciplines during his bicentennial year. Electrochemistry, perhaps more than any other science, can trace its origins directly to Faraday. He established many of its basic laws and originated nomenclature that is still used. Moreover, Faraday showed that research done with the goal of satisfying intellectual curiosity can have great practical benefits.

To this day, electrochemistry is a discipline that is very strong in both its scientific and its technological aspects. The strength of the intellectual and the practical branches of electrochemistry is illustrated in this issue. The papers here, a sampling of electrochemical research in IBM, range from a fundamental examination of the nature of the electrode–electrolyte interface to the understanding of technologically important processes like electroplating. The scope of a single issue does not permit a comprehensive examination of electrochemistry within IBM. Nevertheless, this issue should give the reader an understanding of the contributions that electrochemistry makes to computer technology and of the contributions that IBM has made to electrochemistry.

Electrochemistry is a surface science or, more precisely, an interfacial science. As the dimensions of computer components have become smaller, the role of interfaces has become increasingly important. The solid–vacuum interface has been thoroughly studied, especially within the electronics industry. Electrochemical interfaces have complexities not usually encountered at solid–vacuum interfaces. The solid of interest is most usually a metal or semiconductor; at the other side of the interface is a medium, usually a liquid, in which charge is conducted by ionic species. The distribution of charge across the solid–liquid boundary causes the interface to act like a very thin capacitor. Additionally, the ionic and non-ionic species can assume a complex structure at the interface: They can become oriented by the field at the surface, they can lose waters of hydration, and they can be adsorbed on the surface. Charge can cross the interface, causing a change of physical state.

This issue begins with five papers dealing with the two electrochemical methods of depositing metallic films: electroplating and electroless deposition. Electroplating is one of the most common industrial electrochemical processes; although it has been exploited for many decades, it still provides ample scope for research and development, especially in high-technology applications.

Alloy films have important applications in microelectronics. The papers of Deligianni and Romankiw and of Horkans et al. are concerned with the electroplating of alloys. Permalloy, an alloy of nickel and iron, is useful to the computer industry because of its magnetic properties. It is employed as the magnetic material in plated thin-film inductive heads in storage products. The mechanism of Permalloy deposition, however, is complicated by the co-evolution of hydrogen during the plating. Deligianni and Romankiw have developed a technique for measuring the surface pH rise concomitant with hydrogen evolution during plating. The role of hydrolyzed species in the deposition mechanism can be assessed on the basis of their measurements. The deposition of a very different alloy, tin–lead, has been examined by Horkans et al. In IBM processors, tiny balls of tin–lead form the solder interconnections between chips and packages. Electroanalytical techniques have been developed and used to study tin–lead deposition and the influence of organic addition agents on the composition and morphology of the alloy deposit. Electroanalytical techniques like those described by Horkans et al. are useful for the control of plating processes in a manufacturing environment.

Microelectronic devices commonly require patterned thin films. An advantage of electrochemical deposition methods is that they can be used to deposit metal films directly in patterns. Electroless deposition, because it does not require electrical contact, provides a further advantage in depositing patterned metal films. It exploits an understanding of interfacial chemistry and catalysis at surfaces; the electrons required to deposit the metal film are provided by a reducing agent in solution, and the deposition of the patterned film is achieved by a catalyst present on the surface only where the deposit is needed. The papers by Gaudiello and Ballard and by Jagannathan and Krishnan deal with electroless deposition of copper. Traditional electroless deposition of copper conductors has two drawbacks: The usual reducing agent, formaldehyde, has come under environmental regulation; and the high pH required is incompatible with the insulating materials used. Gaudiello and Ballard have been able to replace the formaldehyde reducing agent and lower the pH by understanding and exploiting the catalytic nature of electroless deposition. Jagannathan and Krishnan have manipulated the chemistry of the complexing agents in solution to allow replacement of formaldehyde in low-pH electroless copper deposition.

The papers of Dukovic and of Moreno et al. use computer modeling to describe and to optimize manufacturing processes. Dukovic has modeled electroplating through patterned resist masks. The evolution of the shape of a deposited feature is examined through modeling, and the effects of various deposition

parameters are assessed. Moreno et al. have modeled mass transfer to a surface from an impinging jet of solution. Impinging jets are of interest in connection with the processes of rinsing, etching, and electroplating, and in the developing of photoresists. The uniformity and efficacy of all of these applications depend on uniform mass transport to the surface. The mass transport has been studied and an understanding of jet instabilities and their importance has thus been gained.

Kanazawa and Melroy describe the development of an *in situ* tool that can be used to study electrochemical processes resulting in net changes of mass. The quartz resonator is a venerable tool which has been used for decades to measure the rate of vacuum deposition. It was not understood until recently, however, that it is also useful in a liquid environment. Kanazawa and his co-workers have contributed significantly to the understanding of electrochemical applications of the quartz resonator. His paper with Melroy summarizes the theory of its use and gives examples of its diverse application.

The next three papers deal with oxidation processes at the surface. Brusic et al. discuss possible corrosion during the fabrication of VLSI structures. The corrosion behavior of copper, of aluminum, and of the aluminum–copper alloy used in VLSI wiring has been determined. Contaminants introduced by reactive ion etching and other process steps can cause corrosion of wiring metals. Surface analytical techniques are often combined with electrochemical measurements in order to obtain information about the structure and chemistry of the electrode surface; Schrott and Frankel have used a combination of two of these techniques, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy, to study electrochemically formed oxide films. These two techniques give complementary information, as illustrated by a study of oxide formation on aluminum–chromium alloys. Datta reviews the present state of understanding of the high-rate electrodissolution of metals, a process that pertains to electro-etching technology. Electro-etching performance is determined by the electrochemical and hydrodynamic parameters employed. In the computer industry, electrochemical machining and electro-etching are often applied to foils and thin films; in these cases, the use of pulsed-current etching may offer advantages over direct current.

In situ infrared spectroscopy is another powerful analytical technique for studying the structure of the electrode–electrolyte interface. Seki reviews electrochemical infrared spectroscopy studies carried out by himself and his colleagues. This work has led to specific knowledge about the adsorption at the electrochemical interface of several species having fundamental electrochemical importance and about the potential dependence of adsorption.

The final two papers in the issue show the importance of electrochemical mechanisms in environments other than the traditional metal–electrolyte interface. White has used electrochemical impedance techniques to identify conduction mechanisms on printed circuit boards contaminated with flux residues. Hydrophobic and water-soluble fluxes result in different conduction mechanisms. The data obtained can be used to predict the performance of boards under expected environmental conditions. Diaz and Guay describe surface charging, which is exploited for copying and printing processes. The mechanism of charging of organic materials, which can be by either ions or electrons, is not well understood. The examination of a variety of organic materials with different structures leads to an elucidation of the charging mechanism.

The practice of electrochemical science and technology, as illustrated in the sampling of papers in this issue, crosses several disciplines—chemistry, physics, engineering, materials science, and surface science. Its use in the computer industry spans many applications—chips, packages and circuit boards, interconnections, heads and media for magnetic recording, and others. In all likelihood, this discipline, whose founder was born more than 200 years ago, will be vital to microelectronics technology even as it continues to evolve; electrochemists will no doubt be celebrating many more Faraday anniversaries.

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